

# Hydrogen Production from Steam Reforming of Acetic Acid as a Model Compound of the Aqueous Fraction of Microalgae HTL Using Co-M/SBA-15 (M: Cu, Ag, Ce, Cr) Catalysts

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Received: 30 October 2019; Accepted: 28 November 2019; Published: 2 December 2019

**Abstract:** Hydrogen production derived from thermochemical processing of biomass is becoming an interesting alternative to conventional routes using fossil fuels. In this sense, steam reforming of the aqueous fraction of microalgae hydrothermal liquefaction (HTL) is a promising option for renewable hydrogen production. Since the HTL aqueous fraction is a complex mixture, acetic acid has been chosen as model compound. This work studies the modification of Co/SBA-15 catalyst incorporating a second metal leading to Co-M/SBA-15 (M: Cu, Ag, Ce and Cr). All catalysts were characterized by N<sub>2</sub> physisorption, ICP-AES, XRD, TEM, H<sub>2</sub>-TPR, H<sub>2</sub>-TPD and Raman spectroscopy. The characterization results evidenced that Cu and Ag incorporation decreased the cobalt oxides reduction temperatures, while Cr addition led to smaller Co<sup>0</sup> crystallites better dispersed on the support. Catalytic tests done at 600 °C, showed that Co-Cr/SBA-15 sample gave hydrogen selectivity values above 70 mol % with a significant reduction in coke deposition.

**Keywords:** microalgae; acetic acid; steam reforming; hydrogen; cobalt; mesostructured materials

## 1. Introduction

An increase in global pollution has resulted in a search for alternative energy resources that can be substituted in place of widely used fossil fuels [1]. It is known that energy provided from hydrogen does not result in pollutant emissions when it is used in fuel cell applications [2–4]. In addition, hydrogen is extensively used in chemical and petroleum industries [5,6]. Nowadays, a hydrogen-based energy system must use renewable energy sources to be sustainable. In this sense, hydrogen production processes such as biomass gasification, and steam reforming (SR) of pyrolysis bio-oil have been widely described in the literature [7–10]. However, the use of microalgae hydrothermal liquefaction integrated with the steam reforming of the aqueous fraction is less known. Microalgae HTL requires temperatures between 250–350 °C and high pressures that can maintain the water coming from the microalgae crops in liquid state (40–250 bar). This process provides a great advantage when compared to the traditional biomass pyrolysis process, as it does not require a previous stage for biomass drying associated with high energy consumption [11–13]. Microalgae HTL products are a complex mixture of different compounds where carboxylic acids, ketones, phenols, aldehydes, fatty acids and nitrogen compounds [14] can be easily found along with a high water content. For this reason, they are not suitable for use as a fuel. However, this worthless aqueous fraction can be revalorized by hydrogen production through catalytic steam reforming [15,16] but the

complex composition mentioned above usually forces the use of model compounds [17–20]. Among them, acetic acid is a major component, which can account even for the 56% of the water-soluble products [17]. The overall equation of the acetic acid steam reforming is:



Nowadays, SR catalysts are a critical point of study where activity, hydrogen selectivity and deactivation are the main concerns of the scientific community. Many papers can be found using different active phases such as Ni, Co, Pt or Ru, with Ni being the most studied [21]. Hu et al. [22] studied the performance of different transition metals supported over  $\text{Al}_2\text{O}_3$  in acetic acid steam reforming. Their study led to the conclusion that Ni and Co were more active than the other metals tested (Fe and Cu). They attributed this behavior to the ability for cracking not only C-C bonds, but also C-H bonds. However, Co-based catalysts have been less reported despite the fact that they also provide high activity at moderate temperatures and also increases hydrogen yield [23,24].

Catalysts support selection is also an important point. For example, when Co was supported on  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  high metal dispersion was reported but cobalt aluminates or titanates were formed avoiding the reduction of some Co species [25]. On the other hand, the interaction of Co with silica has been studied leading to the conclusion that this support does not affect to its reducibility but instead promote the sintering of cobalt particles in the calcination and reduction steps [26,27]. Apart from that, there are other advanced supports such as SBA-15, which is a mesostructured material with high surface area that may allow higher metal dispersion when compared with the amorphous silica. Furthermore, SBA-15 presents an uniform distribution of mesopores that hinders the formation of Co agglomerates preventing also catalysts deactivation due to metal sintering [28].

Co-based catalysts have shown deactivation through sintering and surface cobalt oxidation [21]. Pereira et al. [29] proposed the preparation of bimetallic catalysts to stabilize Co/ $\text{SiO}_2$  catalyst to safeguard the Co particles in a reduced state during the reforming. Combining diverse metals in the same carrier has been reported as an effective way to improve the catalyst performance by facilitating the metal reducibility [30]. As reducibility promoters noble metals, transition metals or  $\text{CeO}_2$  among others can be used. Wang et al. [31] reported that Cu addition to Ni/attapulgit catalyst decreased the temperature for the reduction of nickel species. In line with this, Eschemann et al. [32] proved the efficiency of silver as a reduction promoter in Co/ $\text{TiO}_2$  catalyst since Co-Ag bonds improve the reducibility of cobalt oxides [32,33]. Besides, Harun et al. [34] achieved better  $\text{Ni}^0$  dispersion over  $\text{Al}_2\text{O}_3$  surface when Ag was included in the catalyst formulation. Similarly, it was described that  $\text{CeO}_2$  presents a synergistic effect with cobalt oxides since more oxygen vacancies are formed leading to higher reducibility [35]. In addition to promoting the cobalt reducibility to avoid possible crystallites oxidation, it is necessary to obtain a small crystallite size in order to increase activity and reduce the coke formation according to its growth mechanism [36]. Accordingly, Cerdá-Moreno et al. [37] found that lower Co particle size for ethanol steam reforming led to better catalytic activity. Recently, we have found that Ni-Cr/SBA-15 showed better catalytic behavior than Ni/SBA-15 in the steam reforming of pyrolysis bio-oil aqueous fraction by decreasing  $\text{Ni}^0$  particles size [38]. Furthermore, Casanovas et al. [39,40] reported that the incorporation of Cr to Co/ZnO samples results in better catalytic performance when these catalysts were tested in ethanol steam reforming.

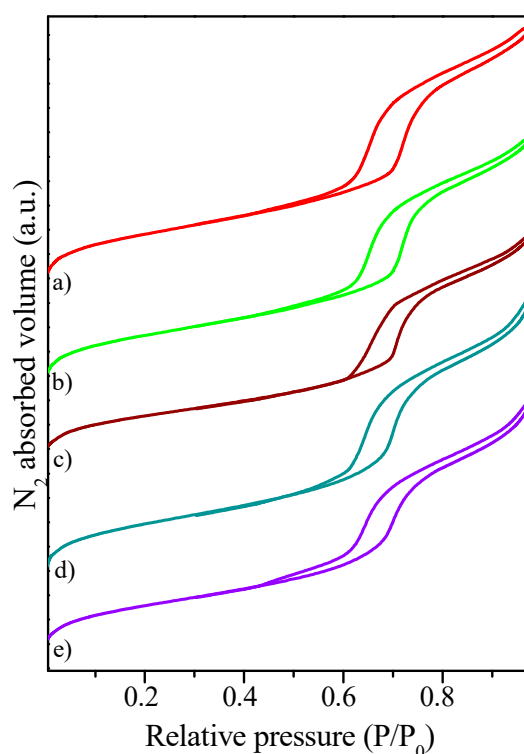
So far, we have not been able to find any references using the promoters described above in Co/SBA-15 catalysts to be tested in acetic acid steam reforming. Therefore, the main goal of this study is the preparation of novel cobalt catalysts incorporating a second metal leading to Co-M/SBA-15 (M: Cu, Ag, Ce and Cr) to achieve high hydrogen production rate through acetic acid steam reforming as model compound of microalgae HTL aqueous fraction.

## 2. Results and Discussion

### 2.1. Catalysts Characterization

Nitrogen physisorption profiles displayed in Figure 1 show type IV isotherms with a H1-type hysteresis loop according to the IUPAC classification, indicating the preservation of the initial

mesostructure of SBA-15 used as the support of these samples. Textural properties calculated from these analyses are summarized in Table 1 along with other physicochemical properties.



**Figure 1.** N<sub>2</sub> physisorption isotherms of calcined (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 catalysts at 77K.

**Table 1.** Physicochemical properties of Co-M/SBA-15 (M: Cu, Ag, Ce, Cr) catalysts.

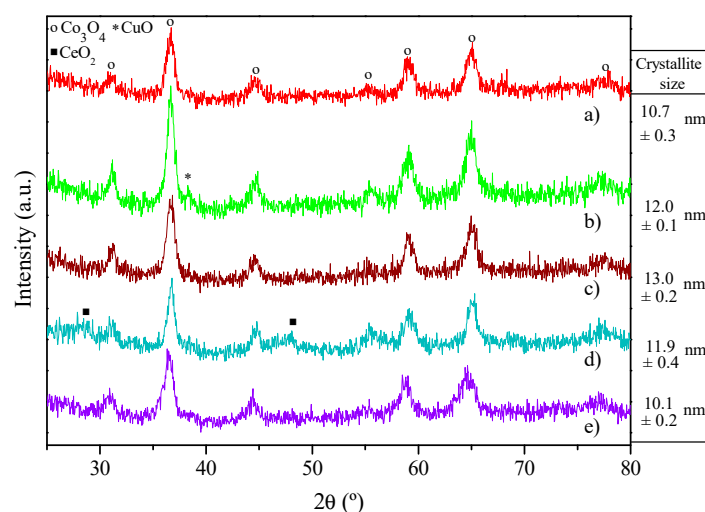
Catalyst	Co <sup>a</sup> (wt.%)	M <sup>a</sup> (wt.%)	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>−1</sup> )	D <sub>pore</sub> <sup>b</sup> (nm)	V <sub>pore</sub> <sup>c</sup> (cm <sup>3</sup> ·g <sup>−1</sup> )	D <sub>Co</sub> <sup>0</sup> <sup>d</sup> (nm)	Dispersion (%) <sup>e</sup>
SBA-15	–	–	550 ± 3	7.5 ± 0.1	0.97 ± 0.02	–	–
Co/SBA-15	6.4 ± 0.1	–	503 ± 4	7.2 ± 0.1	0.83 ± 0.01	9.5 ± 0.5	7.5 ± 0.2
Co-Cu/SBA-15	6.5 ± 0.1	2.0 ± 0.1	476 ± 4	7.2 ± 0.1	0.79 ± 0.03	9.7 ± 0.3	6.3 ± 0.1
Co-Ag/SBA-15	6.4 ± 0.1	1.6 ± 0.1	419 ± 4	6.9 ± 0.1	0.71 ± 0.01	12.3 ± 0.4	3.9 ± 0.6
Co-Ce/SBA-15	6.6 ± 0.1	1.7 ± 0.1	494 ± 1	7.4 ± 0.1	0.84 ± 0.01	9.6 ± 0.2	6.5 ± 0.1
Co-Cr/SBA-15	6.8 ± 0.1	1.8 ± 0.1	469 ± 1	7.1 ± 0.1	0.81 ± 0.02	7.2 ± 0.1	9.9 ± 0.3

<sup>a</sup> Determined by ICP-AES (M: Cu, Ag, Ce or Cr) in reduced samples, <sup>b</sup> BJH desorption average pore diameter, <sup>c</sup> Measured at P/P<sub>0</sub> = 0.97, <sup>d</sup> Determined from XRD of reduced catalysts by Scherrer equation from the (111) diffraction plane of Co<sup>0</sup>, <sup>e</sup> Determined from H<sub>2</sub>-TPD results using formula from Li et al. [41] assuming H/Co = 1.

The metals loading is close to the nominal value used during the catalysts preparation. Metal addition to bare SBA-15 leads to a decrease in BET surface area with Co-Ag/SBA-15 being the sample with the smallest pore size, pore volume and surface area. This phenomena has been described previously [42] and was ascribed to Ag structures growing in the mesopores of SBA-15. Similar textural properties were found in Co-(Cu, Ce or Cr)/SBA-15 samples.

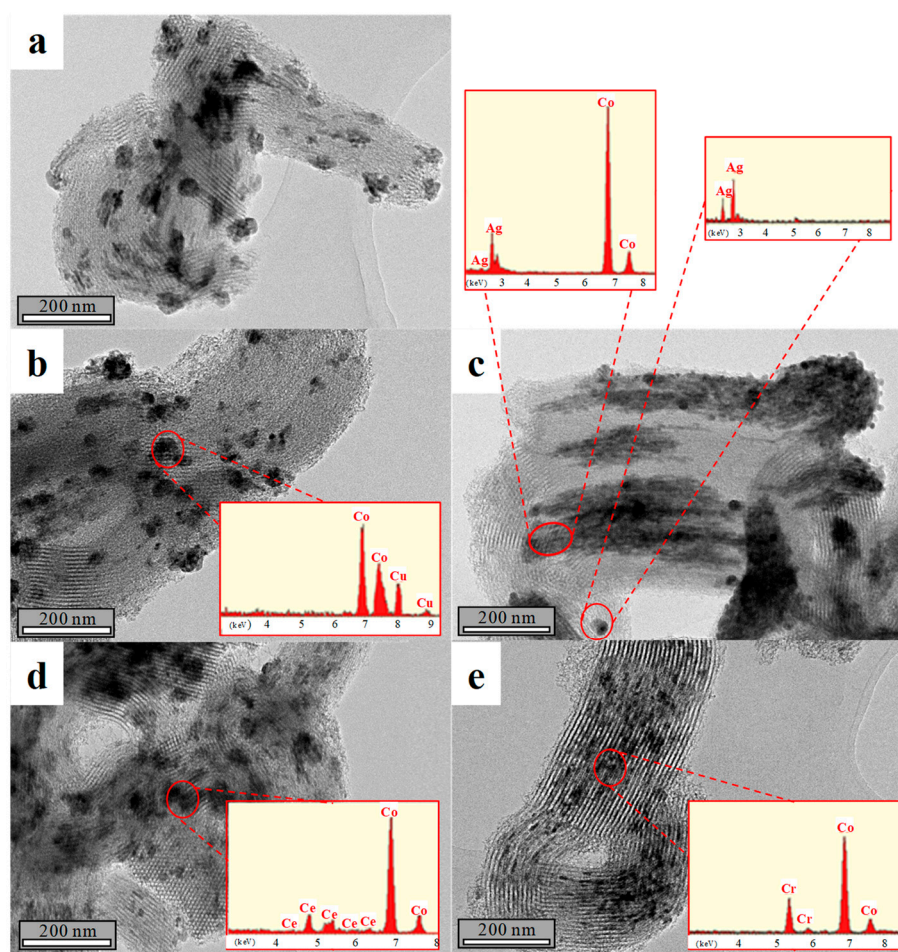
Figure 2 shows the XRD patterns of the calcined samples. Peaks corresponding to cubic Co<sub>3</sub>O<sub>4</sub> appear in all samples (JCDPS 01-071-4921). Attending to Co-Cu/SBA-15 sample, a small peak at 38.3° can be observed due to the formation of monoclinic CuO (JCDPS 01-089-2531). In case of Co-Ce/SBA-15, two small peaks over 28.5° and 47.5° can be seen due to the presence of cubic CeO<sub>2</sub> (JCDPS 01-089-8436). Ag and Cr oxides were not detected by XRD due to the overlap of the main diffraction peaks of cubic Ag<sub>2</sub>O (JCPDS 00-012-0793), rhombohedral Cr<sub>2</sub>O<sub>3</sub> (JCPDS 00-002-1362) and cubic CoCr<sub>2</sub>O<sub>4</sub> spinel (JCPDS 00-022-1084), with the Co<sub>3</sub>O<sub>4</sub> pattern. The higher Co content compared

to Ag and Cr also contributes to the non-detection of Ag and Cr oxides by XRD as were observed in previous works [43,44]. XRD patterns corresponding to Co-(Cu, Ag or Ce)/SBA-15 present narrower  $\text{Co}_3\text{O}_4$  peaks and slightly larger  $\text{Co}_3\text{O}_4$  crystallites were obtained comparing when compared to Co/SBA-15 sample.



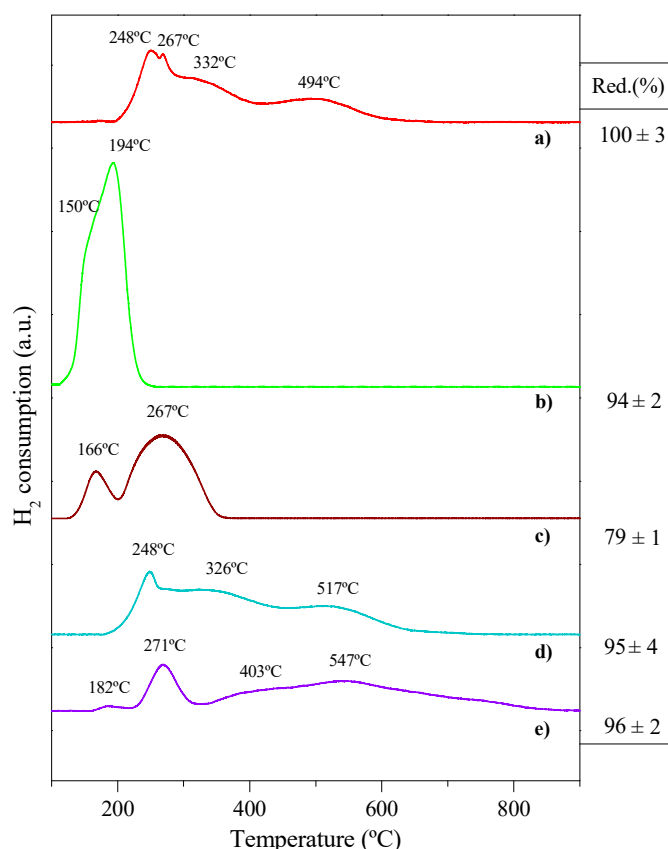
**Figure 2.** XRD of calcined (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 catalysts.  $\text{Co}_3\text{O}_4$  crystallites sizes calculated from the (311) diffraction plane using Scherrer equation are displayed on the right.

Figure 3 shows the TEM micrographs of calcined samples. Irregular metal oxides particles can be observed, some of them formed in the channels of SBA-15, while other particles were formed over the external surface as previously reported [43]. The presence of Co and promoters (Cu, Ag, Ce or Cr) were evaluated in the corresponding sample by EDX indicating an intimate contact between Co oxide and promoters. Co-Ag/SBA-15 catalyst has large metallic nanostructures through the SBA-15 channels and  $\text{Ag}_2\text{O}$  particles can be also observed over the support [45]. The incorporation of high Ag loadings (> 1wt. %) affects support structure and distribution of  $\text{Ag}_2\text{O}$  particles over the catalyst because the probability of Ag-Ag bond formation increases [32,33]. On the other side, it is noticeable how Co-Cr/SBA-15 sample clearly shows the highest dispersion over the support with very small metal oxide particles, which is in agreement with the lower metal diameter calculated from XRD (Table 1).



**Figure 3.** TEM micrographs of calcined samples (a): Co/SBA-15; (b): Co-Cu/SBA-15; (c): Co-Ag/SBA-15; (d): Co-Ce/SBA-15; (e): Co-Cr/SBA-15.

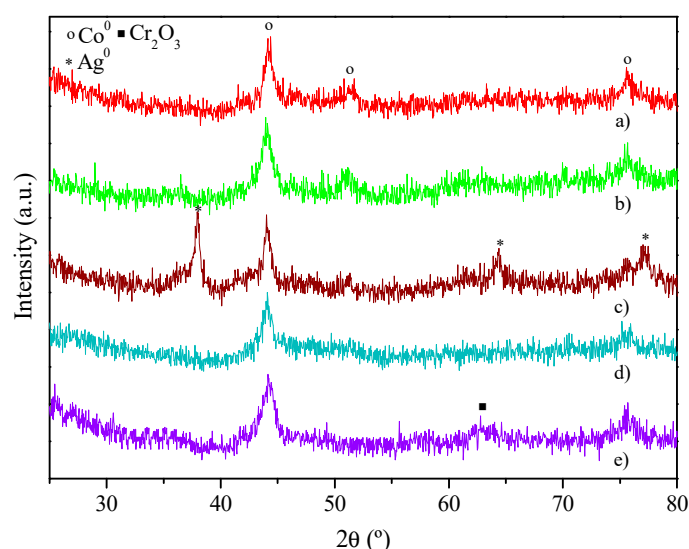
Figure 4 displays the  $H_2$ -TPR profiles of the calcined catalysts. In the case of Co/SBA-15 sample, the reduction profile shows two main reduction stages. The first one with maxima found at 248–267 °C and a shoulder around 332 °C. These peaks are attributed to the reduction of  $Co_3O_4$  to CoO and subsequently to  $Co^0$ . The reduction stage at high temperature, with a maximum placed at 494 °C, can be attributed to the presence of Co-oxide species with stronger interaction with the support [46]. Cu addition led to a clear decrease of the reduction temperature as observed in Co-Cu/SBA-15 profile.



**Figure 4.** H<sub>2</sub>-TPR profiles for (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 samples. Red. (%) data displayed on the right correspond to reducibility.

The reduction zone is located at temperatures between 140–260 °C with two maxima at 150 and 194 °C. Whereas the lower temperature peak is ascribed to the simultaneous reduction of CuO and Co<sub>3</sub>O<sub>4</sub> to Cu<sup>0</sup> and Co<sup>0</sup> respectively, the other one is related to the reduction of CoO to Co<sup>0</sup> [47]. This effect of Cu in lowering reduction temperature of metal oxides was observed in previous works for Ni-based catalysts [43]. Co-Ag/SBA-15 catalyst showed two clearly different reduction areas, also at low temperature. While the zone over 267 °C is related to the Co oxides next to Ag, the other one around 166 °C is attributed to the reduction of segregated Ag<sub>2</sub>O particles to Ag<sup>0</sup> [48]. On the other hand, Co-Ce/SBA-15 sample showed a reduction profile similar to Co/SBA-15 with the peak at 494 °C shifted to higher reduction temperature due to an emerging peak assigned to superficial cerium oxide [49]. Finally, in the reduction profile of Co-Cr/SBA-15 had a new peak around 182 °C, probably due to the reduction of Cr-oxides to Cr<sup>3+</sup> which can be affected by the presence of Co<sub>3</sub>O<sub>4</sub> [50] although it could not be detected by XRD. The peak attributed to Co<sub>3</sub>O<sub>4</sub> reduction at 271 °C remained unaltered whereas the peak of CoO reduction shifts to higher temperatures due to the presence of Cr species [51] or to the confinement of Co oxides into SBA-15 channels because of their smaller size. Based on the literature, the most likely option is the formation of a cobalt chromate mixed oxide [52], although none could be detected by XRD due to the overlap of the main diffraction lines of CoCr<sub>2</sub>O<sub>4</sub> with those of Co<sub>3</sub>O<sub>4</sub>. The XRD patterns of the samples after reduction at 700 °C under pure H<sub>2</sub> flow are displayed in Figure 5. No peaks ascribed to Co<sub>3</sub>O<sub>4</sub> pattern can be detected whereas cubic Co<sup>0</sup> (JCDPS 00-001-1259) peaks corresponding to (111), (200) and (220) planes showing the reflection at 2θ = 44.4°, 51.3° and 75.4° can be observed in all samples after the reduction process.



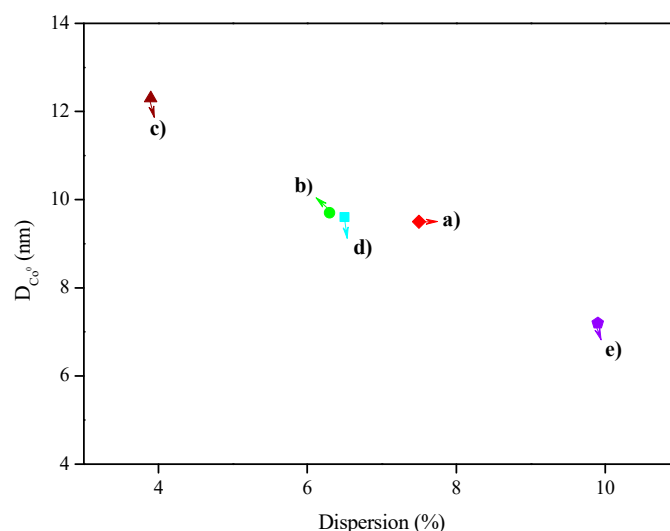


**Figure 5.** XRD of reduced (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 catalysts at 700 °C.

Cubic Ag<sup>0</sup> (JCDPS 00-043-1038) diffraction peaks arose in the Co-Ag/SBA-15 sample at  $2\theta = 38.1^\circ$ ,  $64.5^\circ$  and  $77^\circ$ , ascribed to (111), (200) and (220) reflection planes, respectively. In this case, some Co-oxides could remain in this sample explaining its low reducibility (see Figure 4) but they were not detected because there is an overlapping between Ag<sup>0</sup> and Co<sub>3</sub>O<sub>4</sub> patterns at  $38.1^\circ$  and  $64.5^\circ$ . In Co-Cr/SBA-15 catalyst a peak placed at  $2\theta = 63.7^\circ$  was assigned to rhombohedral Cr<sub>2</sub>O<sub>3</sub> (JCDPS 00-002-1362) probably coming from the release of CoO from the spinel CoCr<sub>2</sub>O<sub>4</sub>. No diffraction peaks of cubic Cu<sup>0</sup> (JCPDS 00-001-1241) were distinguished in Co-Cu/SBA-15 sample due to the overlapping between Cu<sup>0</sup> and Co<sup>0</sup> diffraction peaks. Co-Ce/SBA-15 reduced sample showed only the diffraction peak of metallic Co. The absence of CeO<sub>2</sub> diffraction peaks prompted us to think about the formation of a non-stoichiometric CeO<sub>2-x</sub> that cannot be detected by XRD [53].

Co<sup>0</sup> crystallite sizes were calculated by the Scherrer equation from the diffraction plane (111). In general, whereas Co-Cu/SBA-15 and Co-Ce/SBA-15 samples present a crystallite size similar to Co/SBA-15, Co-Ag/SBA-15 had the largest crystallites (see Table 1) which differs from the literature as silver loading in Co-Ag/SBA-15 is higher than in references [31,32]. In contrast, Co-Cr/SBA-15 presented the lowest Co crystallite size because making a parallelism with the paper of Amin et al. [54] Cr-oxides can suppress the extension growth of Cu-oxides in that case, Co-oxides in our case.

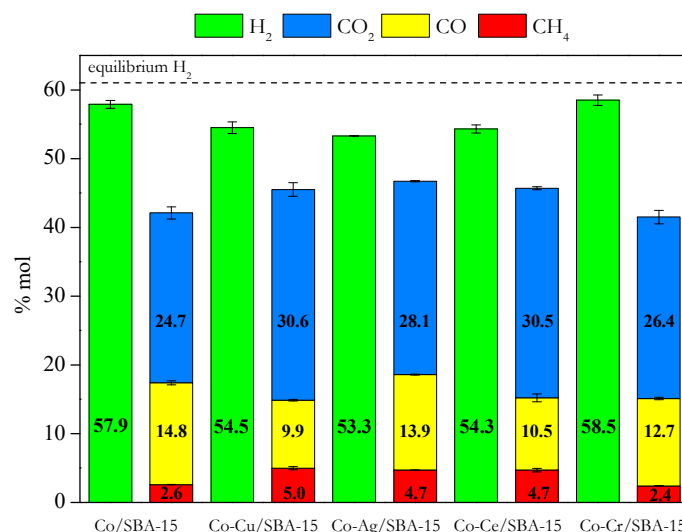
H<sub>2</sub>-TPD analysis was carried out in order to measure the dispersion of the metallic phase over the support. The results, summarized in Table 1, follow the opposite trend as Co<sup>0</sup> crystallite sizes calculated from the Scherrer equation. Co-Cr/SBA-15 sample reached the highest active phase dispersion over the support. This effect can be clearly observed in Figure 6, where Co<sup>0</sup> crystallite sizes are displayed against dispersion and it is clear that the only promoter that improves the base Co/SBA-15 catalyst is Cr. In addition, other authors have reported smaller crystallite size when Cr was incorporated to the catalyst formulation suggesting the capacity of Cr<sub>2</sub>O<sub>3</sub> to act as a textural promoter preventing metallic sintering [55–57]. It should be noted that in a previous work we reported the same behavior with Ni-Cr/SBA-15 sample [38,43], in line with the results obtained by Xu et al. during the co-impregnation of Cr and Ni over char as support [58].



**Figure 6.** Comparison between  $Co^0$  crystallites size and Dispersion over the SBA-15 material used as support for (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15.

## 2.2. Catalytic Tests

AASR (acetic acid steam reforming) reactions were carried out after the reduction of the catalysts. All experiments were performed using an aqueous solution of acetic acid with a S/C molar ratio = 2 and a WHSV = 30.1 h<sup>-1</sup> at atmospheric pressure and 600 °C using N<sub>2</sub> as carrier gas. Conversion data are not shown because all catalysts reached complete conversion along 5 h of time-on-stream, which implies high activity for all the samples in acetic acid conversion at these reaction conditions. However, different product distributions were achieved indicating different activities in acetic acid steam reforming reaction, ascribed to the role of a second metal in secondary reactions. In this sense, hydrogen and carbon co-products distribution (dry basis) are displayed in Figure 7.



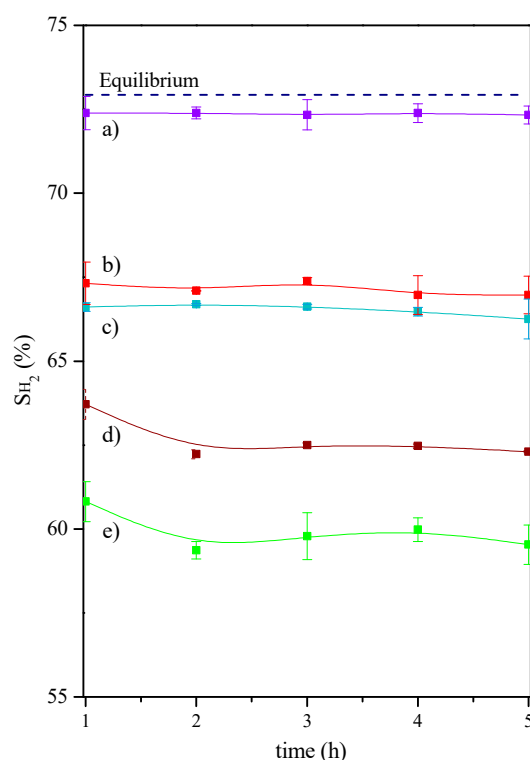
**Figure 7.** Products distribution in outlet gas stream produced in the acetic acid steam reforming over Co-M/SBA-15 (M: Cu, Ag, Ce, Cr) catalysts at T = 600 °C, P = 1 atm, time-on-stream = 5 h.

The H<sub>2</sub> content expected at equilibrium at the experimental conditions, predicted by means of the software GasEQ, based on the method of free Gibbs energy minimization, is also shown. Regarding products distribution, all catalysts reached high hydrogen concentration, above 53%. As known, Co-based catalysts allow the breaking of C-C bonds (only methane is produced as hydrogen-containing product) but also of C-H bonds [22]. Moreover, an effective catalyst must also be active in



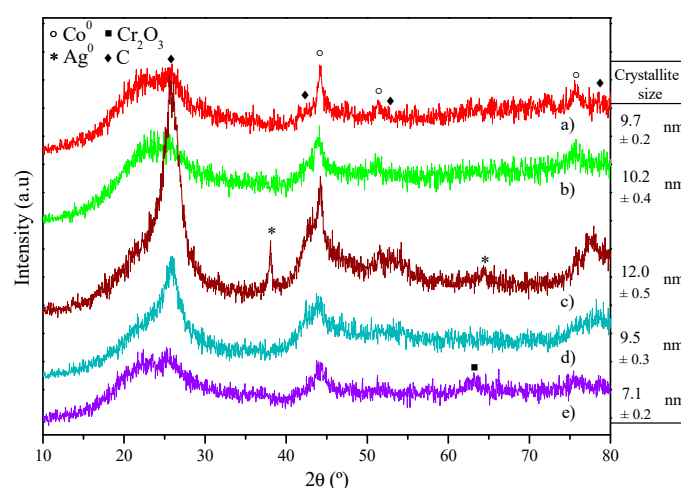
WGS reaction in order to eliminate CO from the metal surface during steam reforming. Over Co, methane reforming and WGS activity was presented and this clearly shown by products formation. Among them, CO<sub>2</sub> formation is highest and followed by CO, CH<sub>4</sub>, thus WGS is more pronounced compared to other disproportionation and decomposition reactions. Cu, Ag and Ce addition to Co/SBA-15 decreases the hydrogen content in the gas outlet stream in line with higher co-carbon products percentages. In contrast, Co-Cr/SBA-15 reached the highest hydrogen concentration in the product stream. This behavior is related to the small Co crystallite size (see Table 1) leading to higher active sites surface area [59,60]. Therefore, Cr addition improved the catalytic performance by preventing Co agglomeration. In fact, Casanovas et al. [40] have published similar behavior adding Cr to Co/ZnO being more active and selective for ethanol steam reforming. On the other side, Co-Ag/SBA-15 achieved the lowest hydrogen concentration and therefore carbon containing products composition was higher, probably due to the pore blocking effect and the highest Co crystallite size. Co-Cu/SBA-15 and Co-Ce/SBA-15 showed higher CO<sub>2</sub>/CO molar ratio compared to the other samples (3/2) suggesting that the activity for WGS reaction was increased [60]. If WGS reaction is favored, an increase in the hydrogen production is expected but the hydrogen content reached with these two catalysts was lower than with Co/SBA-15 (CO<sub>2</sub>/CO ratio = 1.7) thus, it is possible to assume that the presence of a second metal hinders reactants access to Co active centers, thereby avoiding their catalytic role breaking C-H bonds. Finally, Co-Cu/SBA-15, Co-Ag/SBA-15 and Co-Ce/SBA-15 showed an increase of CH<sub>4</sub> from 2% to almost 5% in comparison to the Co/SBA-15 sample. CH<sub>4</sub> formation can be due to the decomposition of acetic acid or methanation [61]. Particularly, Co-Cu/SBA-15 and Co-Ce/SBA-15 produce more CH<sub>4</sub> in line with the reduction of H<sub>2</sub> and CO content which indicates that Cu and Ce promote the methanation reaction ( $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ) [62]. Instead, the increase of produced methane with Co-Ag/SBA-15 could be due to the decomposition of acetic acid since the CO content was kept constant while both CO<sub>2</sub> and CH<sub>4</sub> concentrations increase, which would be in accordance with the stoichiometry of the reaction  $\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$ . However, other parallel and consecutive reactions varying the CO, CO<sub>2</sub> and CH<sub>4</sub> content can be taking place.

Regarding the evolution of H<sub>2</sub> selectivity, calculated as the ratio between hydrogen produced and 4 times the reacted acetic acid (stoichiometry), with reaction time showed in Figure 8 Co-Cu/SBA-15 and Co-Ag/SBA-15 samples exhibited a decrease at 2 h but after that, it remains almost constant. Regardless, the H<sub>2</sub> selectivity of the rest of catalysts remains almost unaltered with time-on-stream. Therefore, no deactivation was detected for Co/SBA-15, Co-Ce/SBA-15 and Co-Cr/SBA-15 samples. In addition, it can be assessed that Co-Cr/SBA-15 sample also achieved the highest H<sub>2</sub> selectivity close to the thermodynamic value at the present reaction conditions. This result is promising compared to those obtained by Ni-based catalysts widely referenced in literature for acetic acid steam reforming reactions. In this sense, Thaicharoensutcharittham et al. [63] reported that Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst with a Ni loading of 5 wt.% reached hydrogen selectivity of 33.54 mol % with a S/C = 1, and 64.39 mol % using a S/C = 3. On the other hand, Wang et al. [64] achieved hydrogen selectivity between 54.5 and 70.9 mol % for reaction tests carried out at 550 °C and 650 °C respectively, with S/C = 3 using Ni/Attapulgate catalysts. In another work, Nogueira et al. [65] published the catalytic performance of Ni catalysts supported on (MgO)-modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reaching, a H<sub>2</sub> selectivity of 67.5 mol % at higher S/C ratio (S/C = 4). Additionally, our group tested at similar operation conditions (600 °C, GHSV: 11000 h<sup>-1</sup>) Ni-based catalysts in AASR with a S/C = 4 [38]. In that work, we achieved up to 60 mol % of hydrogen content for both Ni/SBA-15 and Ni-Cr/SBA-15, which implied H<sub>2</sub> selectivities between 56.6–59.9 mol %. These values are lower than those achieved with Co-M/SBA-15 catalysts in the present work, even though lower S/C ratio has been used that should lead to worse catalytic results. Despite differences in reaction conditions, mainly S/C molar ratio, these H<sub>2</sub> selectivity values are lower than that achieved by Co-Cr/SBA-15 sample. Furthermore, we also observed the beneficial effect of adding Cr to catalysts in our recently published works [38,43], where we reached using Cr as promoter added to Ni/SBA-15 catalysts, better catalytic performance using different feedstock in steam reforming reaction.



**Figure 8.** Hydrogen selectivity of gas stream produced in the acetic acid steam reforming over (a) Co-Cr/SBA-15; (b) Co/SBA-15; (c) Co-Ce/SBA-15; (d) Co-Ag/SBA-15; (e) Co-Cu/SBA-15 catalysts at  $T = 600\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ atm}$ .

Coke formation during steam reforming has been reported as the main cause of SR catalyst deactivation [36]. It must be emphasized that catalyst deactivation is not only related to the amount of coke, but also to the nature of the coke formed, the morphology and the location over the catalyst structure [66]. In this sense, XRD patterns of used catalysts after 5 h (TOS) are shown in Figure 9.

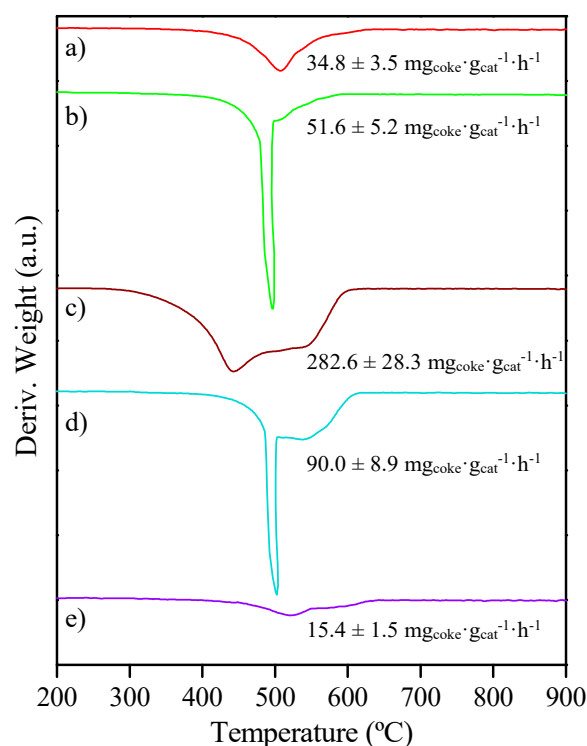


**Figure 9.** XRD patterns of used (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 catalysts.  $\text{Co}^0$  crystallites sizes calculated from the (111) diffraction plane using Scherrer equation are displayed on the right.

Peaks corresponding to cubic  $\text{Co}^0$  (JCDPS 00 001 1259) at  $2\theta = 44.4^{\circ}$ ,  $51.3^{\circ}$  and  $75.4^{\circ}$  can be still distinguished. In contrast to reduced samples (Figure 5), reflection peaks corresponding to graphitic carbon (JCDPS 00-041-1487) at  $2\theta = 26.5^{\circ}$ ,  $42.6^{\circ}$ ,  $53.9^{\circ}$  and  $78.8^{\circ}$  ascribed to (002), (100), (004) and (006) reflection planes, respectively, appear as a consequence of the coke deposition along the acetic acid steam reforming being more pronounced in Co-Ag/SBA-15 sample. Cobalt crystallites sizes of used

catalysts (calculated from Scherrer equation) are shown on the right side of Figure 9. Comparing these results with those found in reduced samples (Table 1), it can be concluded that cobalt crystallites sizes were very similar, which indicates no significant sintering throughout the reforming reaction.

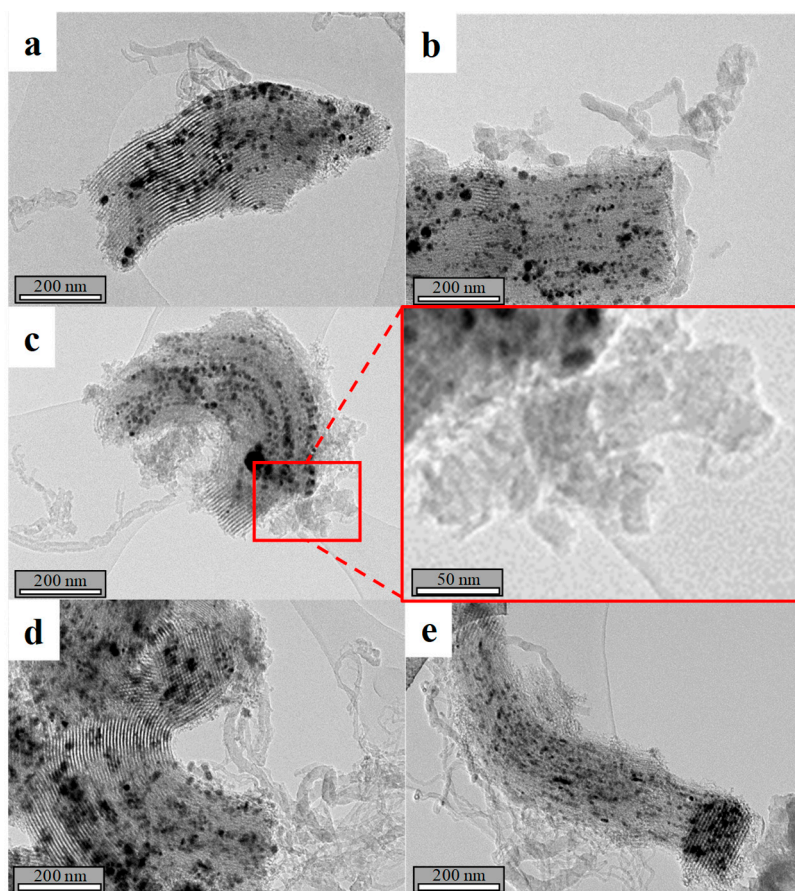
TGA can be used for the identification of the type of coke formed during the reaction since more ordered coke will need higher temperature to be oxidized [67]. It is normally reported that amorphous carbon is more reactive than graphitic in reactions with  $O_2$  [68] because it oxidizes at low temperatures whereas filamentous or graphitic carbon does at higher temperatures [69–71]. Figure 10 displays the derivative thermogravimetric (DTG) curves of the used catalysts along with the amount of coke formed during the reaction in terms of  $mg_{coke} \cdot g_{cat}^{-1} \cdot h^{-1}$ .



**Figure 10.** DTG curves of used (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 samples after 5 h time-on-stream.

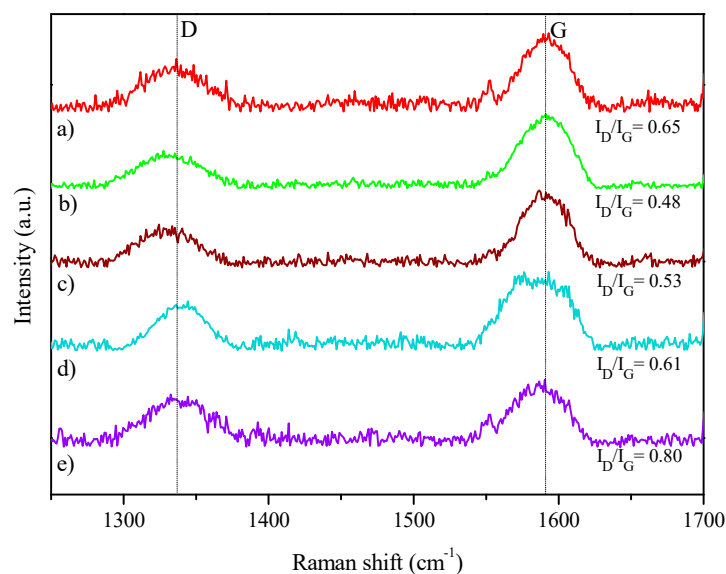
There are significant differences in the total coke content, in the order Co-Ag/SBA-15 > Co-Ce/SBA-15 > Co-Cu/SBA-15 > Co/SBA-15 > Co-Cr/SBA-15 which follows the reverse order of the hydrogen content in the outlet stream during AASR (see Figure 6). In general, all DTG profiles show a maximum around 500 °C and a shoulder around 550 °C, indicating the formation of some kind of carbon nanofibers with different ordering degree [69,70]. Co-Ag/SBA-15 showed a maximum around 441 °C which can be related to the formation of some defective carbon deposits. Co-Ag/SBA-15 obtained the worst catalytic results (high  $CH_4$  concentration and the lowest  $H_2$  concentration), in line with the highest carbon deposition. Besides, it is noteworthy that Co-Cr/SBA-15 reduced the coke production two times compared to Co/SBA-15. It is known that  $Cr_2O_3$  has been used as an oxide catalyst with outstanding carbon deposition resistance properties [72,73]. In our case, the reduction in carbon deposition can be also ascribed to the role of chromium avoiding the formation of large Co crystallites as it could be observed by TEM and measured by the Scherrer equation, because smaller Co crystallites will prevent the initiation of carbon nucleation leading to coke formation [74]. On the other hand,  $Cr_2O_3$  has catalytic activity in the WGS reaction, lowering the CO concentration into the gas phase surrounding the catalytic bed, thus favoring the formation of  $H_2$  and  $CO_2$  [75]. In this sense, the extent Boudouard reaction ( $2 CO (g) \rightarrow CO_2 (g) + C (s)$ ), which is one of the main routes for coking, will be reduced.

Used catalysts were also analyzed by TEM as shown in Figure 11. In all cases, carbon nanofibers with different ordering degree can be observed. Besides, Co-Ag/SBA-15 micrograph shows some zones of defective coke deposits, in concordance with DTG results.



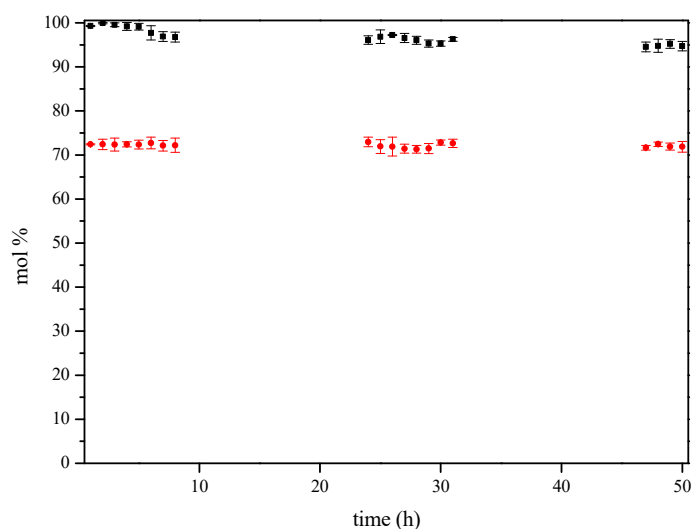
**Figure 11.** TEM micrographs of used (a): Co/SBA-15; (b): Co-Cu/SBA-15; (c): Co-Ag/SBA-15; (d): Co-Ce/SBA-15; (e): Co-Cr/SBA-15 (5 h time-on-stream at 600 °C).

Finally, the Raman spectra of used catalysts in the range 1200–1700  $\text{cm}^{-1}$  are presented in Figure 12. As it can be observed, two main bands appear in all cases, at 1330–1340 ( $\text{D}$ -band) and 1586–1591  $\text{cm}^{-1}$  ( $\text{G}$ -band).  $\text{G}$ -band is ascribed to the stretching mode of carbon  $\text{sp}^2$  bonds of condensed graphitic aromatic structures such as graphite layer [76], whereas  $\text{D}$ -band is related to the carbon atoms vibration of disordered aromatic structures such as amorphous or defective filamentous carbon [70,77–79]. The presence of both bands exhibits the heterogeneity of carbon species constituting the coke formed during the AASR reaction. It has been reported that the intensity of the  $\text{D}$  band relative to the  $\text{G}$  band can be used as a qualitative measure of the formation of different kinds of carbon with different degree of graphitization or disorder in the carbon structure [78–80]. Smaller  $I_{\text{D}}/I_{\text{G}}$  values indicate higher crystallinity due to higher contribution of the graphitic carbon structures formed [81,82] but it also implies more layers constituting the deposited carbon [83]. In these sense, the estimated values are summarized also in Figure 12. As can be seen, the  $I_{\text{D}}/I_{\text{G}}$  ratio decreases in the following order: Co-Cr/SBA-15 ( $I_{\text{D}}/I_{\text{G}} = 0.80$ ) > Co/SBA-15 ( $I_{\text{D}}/I_{\text{G}} = 0.65$ ) > Co-Ce/SBA-15 ( $I_{\text{D}}/I_{\text{G}} = 0.61$ ) > Co-Ag/SBA-15 ( $I_{\text{D}}/I_{\text{G}} = 0.53$ ) > Co-Cu/SBA-15 ( $I_{\text{D}}/I_{\text{G}} = 0.48$ ). These results indicate that carbon deposition over the Co-Cu/SBA-15 sample occurs in larger extent on the Co surface when compared with the other samples, leading to the growth of well-ordered carbon, which may be responsible of catalyst deactivation since it act as a shell covering the active Co sites layer by layer [80]. It must be highlighted that the  $\text{H}_2$  selectivity represented in Figure 8, decreases in the same order as  $I_{\text{D}}/I_{\text{G}}$  ratio. Therefore, the  $\text{H}_2$  selectivity is directly related to the kind of carbon deposited on the catalyst.



**Figure 12.** Raman spectra of used (a) Co/SBA-15; (b) Co-Cu/SBA-15; (c) Co-Ag/SBA-15; (d) Co-Ce/SBA-15; (e) Co-Cr/SBA-15 catalysts.

An AASR test done at long time-on-stream displayed in Figure 13 showed that Co-Cr/SBA-15 achieved good stability after 50 h time-on-stream. Conversion values were near 95% at the end of the reaction, while almost constant hydrogen selectivity (~72 mol %) was obtained. These results evidence that Co-Cr/SBA-15 sample is a promising option for acetic acid steam reforming, since hydrogen selectivity remains close to the equilibrium value for a long period and, in addition, this value is greater than those obtained with the Ni-based catalysts described in literature.



**Figure 13.** Acetic acid conversion (■) and hydrogen selectivity (●) during stability test of Co-Cr/SBA-15 catalyst at T = 600 °C, P = 1 atm.

### 3. Experimental Section

#### 3.1. Catalysts Synthesis

Mesostructured SBA-15 material, synthesized using the hydrothermal method described elsewhere [84], was used as catalysts support. Pluronic 123 and TEOS were used as surfactant and silica precursor (Aldrich, St. Louis, MO, USA) respectively.

Synthesis of Co-M/SBA-15 (M: Cu, Ag, Ce or Cr) catalysts was accomplished by the incipient wetness impregnation method described in previous work [85]. Metal loading was selected as 7 wt. %

of Co and 2 wt.% of promoter [86]. In this way, mixed aqueous solutions of the corresponding nitrates were used for the co-impregnation:  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Acros Organics, Morris Plains, NJ, USA) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{AgNO}_3$  (Aldrich, St. Louis, MO, USA). Subsequently, the prepared samples were calcined under air at 550 °C.

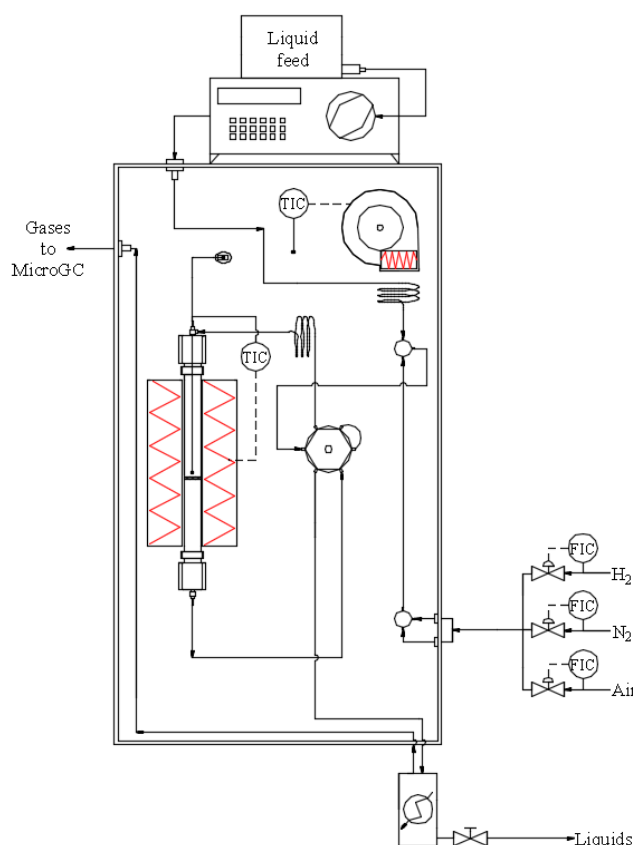
### 3.2. Catalysts Characterization

$\text{N}_2$  adsorption/desorption at 77 K on a TRISTAR 3000 sorptometer (Micromeritics, Norcross, GA, USA) was used for the measurement of textural properties. Prior to the analysis samples were outgassed under vacuum at 200 °C for 4 h. To determine the chemical composition of the catalysts, ICP-AES technique was used. The equipment was a VISTA-PRO AX CCD-Simultaneous ICP-AES spectrophotometer (Varian, Palo Alto, CA, USA). Samples were previously treated by acidic digestion. XRD measurements were recorded using an X'pert PRO diffractometer (Philips, Eindhoven, The Netherlands) using  $\text{Cu K}\alpha$  radiation. The Scherrer equation was used to estimate the metal crystallites mean diameter. Reducibility of the samples was studied by TPR analyses. A Micromeritics (Norcross, GA, USA) AUTOCHEM 2910 system was used. The experiment is carried out flowing 35 N mL/min of gas (10%  $\text{H}_2/\text{Ar}$ ) through the sample and increasing temperature up to 980 °C with a 5 °C/min heating ramp. Samples were previously outgassed under Ar flow at 110 °C for 30 min. Co dispersion of the catalysts was determined by hydrogen TPD in the same apparatus. For that, the samples were first reduced under 35 N mL/min of gas (10%  $\text{H}_2/\text{Ar}$ ), then cooled to 50 °C, and saturated with  $\text{H}_2$ . After that, the physically absorbed  $\text{H}_2$  is removed by flushing Ar and finally heated up to 700 °C at 5 °C/min in Ar flow (30 N mL/min). TEM micrographs were obtained on a 200 kV JEM 2100 microscope (JEOL, Tokyo, Japan), with a resolution of 0.25 nm at the National Centre for Electron Microscopy (CNME, Complutense University of Madrid, Madrid, Spain). It also has the possibility to achieve microanalysis results by energy dispersive X-ray spectroscopy (EDX). Samples preparation involve their suspension in acetone and subsequently deposition on a carbon-coated copper or nickel grid. Carbon deposited during catalytic tests was measured by thermogravimetric analysis (TGA), TEM and Raman spectroscopy. TGA analysis were performed in airflow with a heating rate of 5 °C/min up to 1000 °C on a SDT 2960 thermobalance (TA Instruments, New Castle, DE, USA). Raman spectra were recorded using a NRS-5000/7000 series Raman spectrometer (JASCO, Tokyo, Japan) at the IMDEA Energy Institute.

### 3.3. Catalytic Tests

Acetic acid steam reforming reactions were performed at 600 °C on a MICROACTIVITY-PRO unit (PID Eng. & Tech. S.L., Alcobendas, Madrid, Spain) as described in previous works [7,38,85,87]. The reactor consists in a fixed-bed tubular reactor in stainless steel 316 (i.d. = 9.2 mm, L = 300 mm). The reactor is located inside an electric oven of low thermal, where temperature in the catalytic bed was measured by means of a K-thermocouple. All the components inside the hot box were maintained at 200 °C to prevent condensation in the pipes and to preheat the reactants. A schematic diagram is displayed in Figure 14.





**Figure 14.** Schematic diagram of the catalytic testing setup [38].

The reactions were carried out isothermally at atmospheric pressure. Before tests, all catalysts were reduced under pure hydrogen (30 mL/min) up to 700 °C with a heating rate of 2 °C/min. Temperature was maintained for 30 min. Reaction feed was a mixture of acetic acid and water using a steam to carbon molar ratio of 2, using N<sub>2</sub> as carrier and internal standard (GHSV = 11,000 h<sup>-1</sup>). The composition of the outlet gas was measured online with an 490 Micro-GC (Agilent, Santa Clara, CA, USA) equipped with a thermal conductivity detector (TCD), a PoraPlot U column (10 m) and a Molecular Sieve 5A column (20 m) using He and Ar as carrier gas, respectively. Condensable vapors were trapped in the condenser at 4 °C and analyzed in a Varian (Palo Alto, CA, USA) CP-3900 chromatograph equipped with a CP-WAX 52 CB (30 m × 0.25 mm, DF = 0.25) column and flame ionization detector (FID).

#### 4. Conclusions

The incorporation of a second metal like Cu, Ag, Ce or Cr into Co/SBA-15 sample catalyst resulted in bimetallic catalysts with very different properties and catalytic behavior in acetic acid steam reforming. Co-Ag/SBA-15 presented some pore blockage of the SBA-15 structure due to the presence of isolated silver oxide particles. Cu and Ag addition to Co/SBA-15 led to a significant decrease in the reduction temperature, as shown in H<sub>2</sub>-TPR profiles. Cu addition to Co/SBA-15 favors Co oxide reducibility, while maintaining almost unaltered Co<sup>0</sup> crystallites size. In contrast, Co-Ag/SBA-15 showed also lower reduction temperatures but larger Co<sup>0</sup> crystallites than Co/SBA-15. However, Ce addition does not affect significantly neither reducibility nor Co<sup>0</sup> crystallite size. Finally, Cr addition to Co/SBA-15 strongly decreases Co crystallites size, induced by the presence of chromium oxides, improving metal dispersion with a slight decrease in the reduction temperature.

Regarding acetic acid steam reforming, Co-Cu/SBA-15 and Co-Ag/SBA-15 gave lower hydrogen selectivity than unmodified Co/SBA-15 catalyst. However, Cr addition improved the catalytic behavior reaching the highest hydrogen selectivity next to the thermodynamic equilibrium. After the steam reforming tests, cobalt crystallites sizes in the used catalysts were very similar to those in fresh samples, indicating that coke deposition and not sintering is the cause of catalysts deactivation.

Besides, the amount of coke formed on Co-Cr/SBA-15 was much lower than on the rest of the catalysts after 5 h of time on stream. Another difference resided in the nature of coke deposited because disordered aromatic structures such as amorphous or defective filamentous carbon were formed in a higher extent on Co-Cr/SBA-15 ( $I_b/I_g = 0.80$ ) while the contribution of condensed graphitic aromatic structures increased in Co-Cu/SBA-15 ( $I_b/I_g = 0.48$ ). Thus, Cr addition to Co/SBA-15 resulted in the best catalytic performance on acetic acid steam reforming, but Cr toxicity opens the way to the search for other metals providing similar catalytic properties.

**Author Contributions:** Conceptualization, A.C. and J.A.C.; methodology, A.J.V.; validation, A.J.V.; formal analysis, A.C.; investigation, P.J.M.; writing—original draft preparation, P.J.M.; writing—review and editing, A.C., J.A.C. and A.J.V.; supervision, A.C., J.A.C. and A.J.V.; project administration, A.C. and J.A.C.; funding acquisition, A.C. and J.A.C.

**Funding:** This research was funded by the Spanish Ministry of Economy and Competiveness (project ENE2017-83696-R) and the Regional Government of Madrid (project S2018/EMT-4344).

**Acknowledgments:** The authors acknowledge the IMDEA Energy Institute and the Complutense University of Madrid for the Raman and TEM analyses, respectively.

**Conflicts of Interest:** The authors declare no conflict of interest.

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